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SECTION A

[VOL. 16

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**THERMAL IONIZATION OF ALUMINIUM AND
DETERMINATION OF THE SPECIFIC CHARGE OF Al^+**

By

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NOW IN C. S. I. R. LABORATORIES, DELHI

(Communicated by Dr. B. N. Srivastava, D. Sc.)

ABSTRACT

The thermal ionization of Aluminium has been studied employing the vacuum graphite furnace constructed by Saha and Tandon. The problem is experimentally more difficult than for other elements due to the low vapour pressure and large ionization potential of aluminium, and has necessitated some modification in the usual experimental arrangement. The mean value of the energy of ionization is found to be 135.9 K. cals. which is in good agreement with the spectroscopically determined value within limits of experimental error.

Following the method developed in the paper on lithium the e/m for Al^+ has also been determined by applying the space charge theory to unipolar positive current produced by Al^+ ion. The value obtained is 1.22×10^{13} e. s. u./gm.

I. INTRODUCTION

In the present paper the thermal ionization of aluminium has been studied and the specific charge of Al^+ determined. Similar studies were made with Lithium (Srivastava and Bhatnagar 1946) and calcium (Bhatnagar 1947). A full account of the apparatus

used for the study of thermal ionization has been given by Srivastava (1940). In order to determine the specific charge a strong electromagnet has been recently included in the apparatus. A complete description of the electromagnet, of the experimental procedure for determining the specific charge of ions, and of the theory underlying the method is given in the paper on lithium, (Srivastava and Bhatnagar 1946).

The method is applicable only to unipolar currents, i.e., the currents produced by one type of charged particles. This condition is experimentally realised by deflecting away the electrons from the effusion beam, with the help of the electromagnet. The method gives very satisfactory results, and helps in the identification of the particles producing positive currents in the study of the thermal ionization of elements.

2. THERMAL IONIZATION OF ALUMINIUM.

The problem has greater experimental difficulties than hitherto encountered in our study on the thermal ionization of elements due to the fact that aluminium has a very low vapour pressure and even at temperatures as high as 1500°K of the container in which the element is placed during the experiment, no measurable ionization was produced in the main furnace. After a large number of

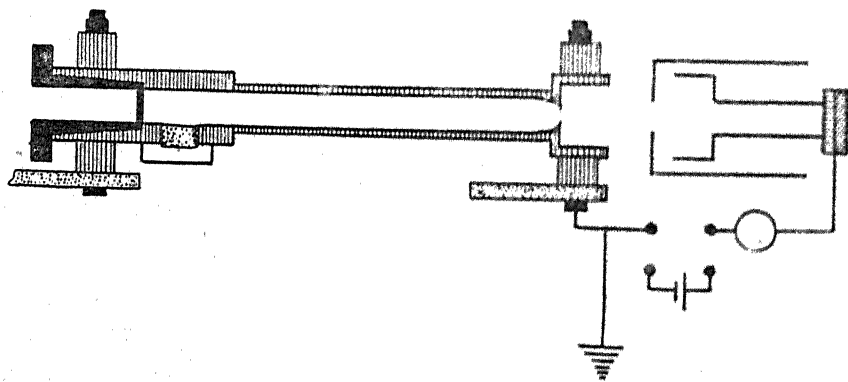


Fig. 1.

trials, it was found that no separate side-tube attached to the main furnace and heated by conduction from the latter, as has been employed so far in all previous experiments, could produce the required temperature. The side furnace was, therefore, dispensed with and in its place, a small plug (see fig. 1) with a shallow cavity in its neck was screwed on to the main furnace such that the substance contained in the cavity was in level with the walls of the main furnace and had the same temperature as that part of the graphite tube.

This portion of the tube is at a lower temperature than the central part of the graphite furnace, but is incandescent enough to enable its temperature to be read with the pyrometer, which has been throughout employed to find the temperature of the main graphite furnace. Aluminium in the form of fine powder was introduced in the cavity at the top of the plug which was then screwed on to the main furnace.

The ionization currents produced by electrons and the positive ions were measured at various temperatures and the corresponding equilibrium constant K calculated with the help of the following relation (See Srivastava 1938 eqn. 15)

$$K = \frac{2\pi kT}{e^2 S^2} \left(\frac{r^2 + d^2}{r^2} \right)^2 \frac{i_g^- i_g^+}{p_a} \frac{\sqrt{m_i \times m_e}}{(1.013 \times 10^6)^2} \quad \dots (1)$$

where r = the radius of the aperture in the limiting diaphragm.

d = the distance between the effusion hole and diaphragm

S = area of the effusion hole, and all other quantities have their usual significance.

The ionization formula

$$\begin{aligned} \log K &= \log \frac{p_i \times p_e}{p_a} \\ &= -\frac{U}{4.573T} + \frac{5}{2} \log T - 6.479 + \log 2 + \log b'(T) - \log b(T), \quad (2) \end{aligned}$$

with the help of (1) then gives U , the energy of ionization per gram atom. The term $b(T)$ comes out to be 2.0000 and $b'(T) = 1.0000$.

The available data on the vapour pressure of aluminium fortunately cover the range of temperature over which observations have been taken in these experiments.

Table I gives the results on the thermal ionization of aluminium. i_g^- and i_g^+ in columns 4 and 5 are the zero-field values of the current obtained as explained in the paper on thermionic work function of graphite (Bhatnagar, 1944). The value of the energy of ionization so obtained agrees well with the spectroscopically determined value.

TABLE I

Radius of effusion hole = 0.8 mm.

Radius of the aperture in the limiting diaphragm = 4.2 mm.

Distance of diaphragm from effusion hole = 18 mm.

Sensitiveness of galvanometer = 1.25×10^{-9} amp./mm.

Temp. of graphite furnace T (Abs)	Temp. of Aux. furnace T (Abs)	$\log p$ in main furnace	i_g^- in mm	i_g^+ in mm	$\log K$ (Atmos)	U in K. eals
1840	1660	1.2223	1500	45	15.7373	134.2
1850	1665	1.2479	1530	30	16.2424	137.4
1863	1675	1.3731	2010	56	15.8142	135.3
1878	1683	1.3987	2280	65	15.9112	135.6
1903	1705	1.5233	4200	83	14.4639	135.3
1908	1705	1.5244	3600	80	14.0810	136.4
1930	1725	1.6244	5100	95	14.2120	136.9

3. DETERMINATION OF e/m .

After the aluminium has been ionised in the main furnace, the products of ionization consisting of electrons and ionised atom effuse out of the effusion hole. The electrons are deflected off from the effusing beam by the electromagnet, as they traverse the path between the effusion hole and the limiting diaphragm, and only the positive ions, which are very little affected by the magnetic field, enter the space between the diaphragm and the Faraday cylinder. The positive ions are collected by the Faraday cylinder which is maintained at a suitable negative potential, and the flow of the positive ions from the diaphragm to the Faraday cylinder constitutes the unipolar positive currents to which the space charge theory may be applied. The currents are measured at various accelerating voltages (see table II) and are given by the relation (Srivastava 1946)

$$i = \frac{\sqrt{2}}{9\pi} \left(\frac{e}{m} \right)^{1/2} \frac{V^{3/2}}{x^2} A \text{ approx.} \quad (3)$$

where x = the interelectrode distance, i.e., the distance between the diaphragm and the Faraday cylinder, and A = the area of the aperture in the limiting diaphragm.

TABLE II

$T = 1850^\circ \text{ K}$, $x = 21 \text{ mm}$, $A = \pi \times (0.42)^2 \text{ sq. cm}$

V in volts	d in mm
0.5	29
1.0	34
1.3	35
1.6	36.5
2.0	39
2.5	41
3.0	44
4.0	49.5
5.0	52

Plotting $i^{2/3}$ against V we get the curve of Fig. 2. The slope of the curve which is equal to

$$\left[\frac{\sqrt{2} \left(\frac{e}{m} \right)^{1/2} A}{9\pi x^2} \right]^{2/3}$$

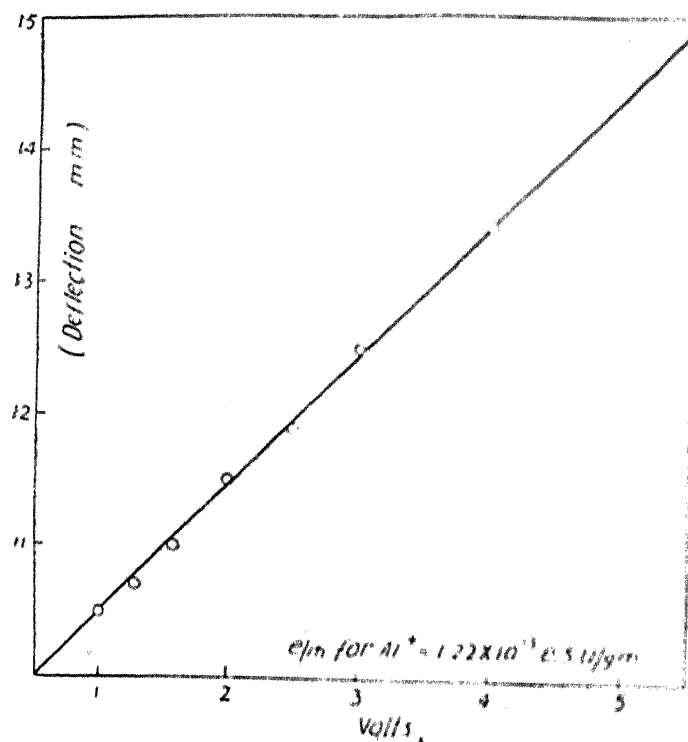


Fig. 2.

from equation (3) then enables us to calculate e/m . The value of e/m so calculated is 1.22 e.s.u./gm which agrees well with the value for Al^+ obtained by direct calculation and establishes beyond doubt that the positive current in the experiment on the thermal ionization of aluminium is due to Al^+ . As shown by Srivastava (1946) this method is capable of yielding values of e/m correct to about 15%.

My sincere thanks are due to Dr. B. N. Srivastava, D.Sc., under whose guidance this work was done at the University of Allahabad.

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STUDY OF THE COMPLEX FORMATION BETWEEN MERCURIC CHLORIDE AND SOLUBLE CHLORIDES BY THE ELECTRICAL CONDUCTIVITY METHOD

PART II - STUDY OF THE HgCl_2 - KCl SYSTEM

By

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(Read at the Annual Meeting of the Academy on 22nd November, 1947)

ABSTRACT

In part I of the series, the compositions of chloromercuric acids have been studied by the electrical conductivity method. In this paper the compositions of chloromercuriates, resulting in the complex formation between mercuric chloride and potassium chloride have been described. The method adopted for the study is the same as followed by the author for the study of various complex forming systems. The conductivity curves give indications of the formation of the following complex compounds: KCl , HgCl_2 ; 2KCl , HgCl_2 and 4KCl , HgCl_2 .

INTRODUCTION

A large amount of work has been carried on the nature of the complex mercuric compounds. In recent years Bhagwat and Toshniwal¹ investigated the behaviour of mercuric chloride in aqueous solutions. Yajnik and Uberoy² adopted some physico-chemical methods for the study of complex formation between mercuric salts and soluble halides, and Pernot³ and Gallais⁴ studied the complex formation in non-aqueous solvents. Samuel and co-workers⁵ studied the complex system by spectroscopy and Nayar and Saraf⁶ investigated the Raman Spectra. Some of the workers are in favour of assigning the formula R_4HgX_4 to the complex formed, whereas others favour HgX_3^- as the formula for the complexion. Thus Krishnamurti⁷,
A 47-3-2

Braune and Englebrecht⁸ and Bernstein and Martin⁹ are in favour of the latter formula for the complex. On the other hand Solanki and Joshi¹⁰ by conductivity, viscosity and refractivity measurements claim to have obtained the evidence for the existence of the following compounds: 10KI, HgCl₂; 20KI, HgCl₂ and 4.5KI, HgCl₂, which however have not been confirmed by other workers.

In view of the conflicting results obtained by various workers we undertook the study of this problem and in Part I of the series¹¹ we have investigated the complex formation between mercuric chloride and hydrochloric acid. In this paper the work has been extended to the study of mercuric chloride-potassium chloride system.

EXPERIMENTAL

Specific conductivity values for solutions of M/200 mercuric chloride of different concentrations of potassium chloride and also for mixtures of various compositions were accurately determined at 30°.

The experimental results are given in the following tables.

Electrical conductivity of M/200 mercuric chloride = 6.343×10^{-6} mhos.

TABLE I

Specific conductivity of potassium chloride at different dilutions.

Concentration				Electrical conductivity in 10^{-3} mhos
M/10	12.84
M/20	6.863
M/30	4.792
M/40	3.537
M/50	2.856

Concentration				Electrical conductivity in 10^{-3} mhos
M/60	2.420
M/70	2.096
M/80	1.798
M/90	1.713
M/100	1.416
M/110	1.329
M/120	1.237
M/140	1.014
M/160	0.9282
M/180	0.8078
M/200	0.7356
M/240	0.6326
M/280	0.5462

TABLE II

Specific conductivity of mixtures of mercuric chloride and potassium chloride of various compositions.

Final concentrations of the constituents in the mixture		Ratio	Specific conductivity in 10^{-3} mhos
HgCl ₂	KCl	HgCl ₂ : KCl	
M/200	M/1	1 : 20.0	13.074
"	M/20	1 : 10.0	6.973

Final concentrations of the constituents in the mixture		Ratio	Specific conductivity in 10^{-3} mols
HgCl ₂	KCl	HgCl ₂ : KCl	
M/200	M/30	1 : 6.67	4.856
"	M/40	1 : 5.00	3.585
"	M/50	1 : 4.00	2.961
"	M/60	1 : 3.33	2.552
"	M/70	1 : 2.86	2.120
"	M/80	1 : 2.50	1.816
"	M/90	1 : 2.22	1.749
"	M/100	1 : 2.00	1.465
"	M/110	1 : 1.82	1.342
"	M/120	1 : 1.67	1.249
"	M/140	1 : 1.43	1.027
"	M/160	1 : 1.25	0.9125
"	M/180	1 : 1.11	0.8221
"	M/200	1 : 1.00	0.7579
"	M/240	1 : 0.83	0.6419
"	M/280	1 : 0.71	0.5545

DISCUSSION OF RESULTS

It is well known that the physical properties of mixtures not yielding complexions are additive. The converse is also true and any change in the physical properties of mixtures is usually due to complex forma-

tion. From the experimental data recorded in this paper the percentage change in electrical conductivity due to the complex formation between mercuric chloride and potassium chloride have been tabulated below.

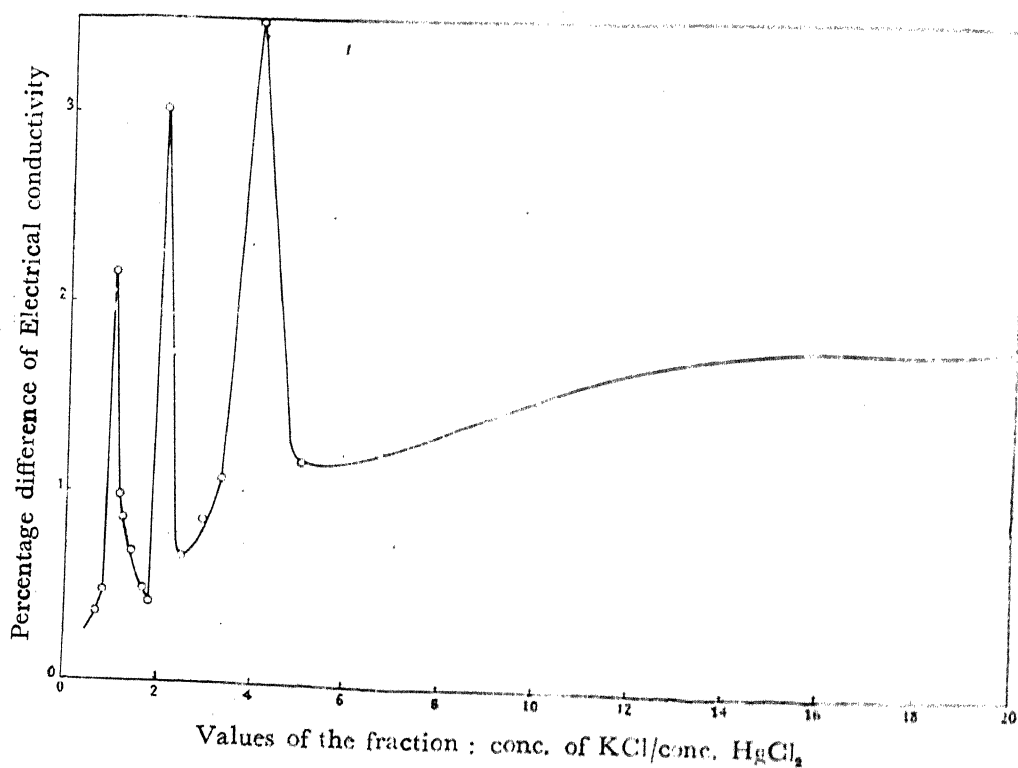
TABLE III

Mixtures of mercuric chloride and potassium chloride

Composition of the mixture HgCl ₂ : KCl	Sum of the conductivities of the constituents in 10 ⁻³ mhos	Observed conductivity of the mixture in 10 ⁻³ mhos	Difference in 10 ⁻⁴ mhos	Percentage difference
1 : 20.0	12.84	13.074	2.34	1.81
1 : 10.0	6.869	6.973	1.04	1.51
1 : 6.67	4.798	4.856	0.58	1.21
1 : 5.00	3.543	3.585	0.43	1.18
1 : 4.00	2.862	2.961	0.99	3.46
1 : 3.33	2.426	2.552	0.26	1.07
1 : 2.86	2.102	2.120	0.18	0.86
1 : 2.50	1.804	1.816	0.12	0.66
1 : 2.22	1.719	1.749	0.30	1.74
1 : 2.00	1.422	1.465	0.43	3.02
1 : 1.82	1.335	1.342	0.07	0.42
1 : 1.69	1.243	1.249	0.06	0.48
1 : 1.43	1.020	1.027	0.07	0.69
1 : 1.25	0.9345	0.9425	0.08	0.86
1 : 1.11	0.8141	0.8221	0.08	0.98
1 : 1.00	0.7419	0.7579	0.16	2.15
1 : 0.83	0.6389	0.6419	0.03	0.47
1 : 0.71	0.5525	0.5545	0.02	0.36

From the above table a graph has been plotted with percentage difference in conductivity against the composition of the mixture. The curve shows sharp breaks corresponding to the following compositions of the mixture : 1KCl , 2KCl and 4KCl for 1 molecule of HgCl_2 . Thus we conclude that the following chloromercuriates are formed by complex formation between mercuric chloride and potassium chloride : KCl , HgCl_2 ; 2KCl , HgCl_2 and 4KCl , HgCl_2 . It will be of interest to remember that in Part I, similar complexes were found to be present in a mixture of mercuric chloride and hydrochloric acid solutions. Some workers have reported the formation of a compound $1/2\text{KCl}$, HgCl_2 , which was not found by us, as we did not work with extremely dilute solutions of potassium chloride. It is likely that this compound may also exist under suitable conditions.

Conductometric Study of HgCl_2 -KCl System



From these studies, I am of opinion, that since several well defined compounds are capable of existence, involving various proportions of mercuric chloride and potassium chloride the wide variation in the compositions of these complexes as found by different workers is quite likely, as their products may easily be a mixture of one or more of such complexes.

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